

Manuscript Title:

Comment on "Layering transition in confined molecular thin films: Nucleation and growth"

Saroj Kumar Nandi*

*Centre for Condensed Matter Theory, Department of Physics,
Indian Institute of Science, Bangalore-560012, India.*

(Dated: February 3, 2008)

When fluid is confined between two molecularly smooth surfaces to a few molecular diameters, it shows a large enhancement of its viscosity. From experiments it seems clear that the fluid is squeezed out layer by layer. A simple solution of the Stokes equation for quasi-two-dimensional confined flow, with the assumption of layer-by-layer flow is found. The results presented here correct those in Phys. Rev. B, **50**, 5590 (1994), and show that both the kinematic viscosity of the confined fluid and the coefficient of surface drag can be obtained from the time dependence of the area squeezed out. Fitting our solution to the available experimental data gives the value of viscosity which is ~ 7 orders of magnitude higher than that in the bulk.

PACS numbers: 68.35.-p, 68.45.-v, 68.15.+e

The observed giant enhancement of viscosity dealing liquids under confinement has led to many experiments [1, 2, 3, 4], computer simulations [5, 6, 7], and some theory [8, 9, 10]. When confined to a spacing of few monolayers between two solid surfaces, fluids start behaving very differently than in the bulk, exhibiting a dramatic increase in viscosity of six to seven orders of magnitude, and perhaps an yield stress [1, 11].

The literature is conflicting on the question whether the observed slowing down of the dynamics in the confined fluid stems from a phase transition [11]. For fluid particles of regular shape, some interpretations show the possibility of surface induced crystallization [12], others of a glass transition [13], both at temperatures well above the respective bulk transition temperature. It is somewhat unsatisfactory, if not strange, that the same basic experiment is interpreted in both terms. One important conclusion can be drawn from these that our theoretical understanding of the phenomenon is not really complete.

In computer simulations, using surfaces with periodicity commensurate with the bulk crystalline phase of the confined fluid, the fluid showed an ability to sustain an applied static stress [12]. But in the simulation of Gao et al [14] with incommensurate surfaces, this does not happen. This shows the importance of commensurability. But the experimental systems studied so far involve confined fluids with a variety of molecular shapes and architecture, and are generally incommensurate with the surfaces. Therefore commensurability is probably not relevant [15]. Actually confinement is a means to introduce geometrical constraints [16] and this slowing down of the dynamics should have a more general origin rather than a mere commensurability.

The high increase in the viscosity is perhaps a result of mode-coupling [18, 19] modified by confinement

[17]. Such a theory is beyond the scope of this work. It is however interesting that a simple phenomenological treatment in the form of layer-by-layer viscous flow gives physically relevant results.

This model introduced here was first considered by Persson and Tosatti[8]. But their solution does not say anything about the kinematic viscosity, since their calculation *seemed* to show that the spreading of the monolayers is determined by the wall-fluid friction, which they have introduced as a separate parameter, and not by the kinematic viscosity of the fluid. In fact the spreading *does* depend on the viscosity, as shown below. The Persson and Tosatti model is thus more interesting than its authors showed it to be. I redo the Persson and Tosatti calculation below with a result different from theirs, and I point out where there was an error in their calculation. The result is important because it shows that a measurement of the time evolution of the area of the squeezed monolayer gives an estimate of the viscosity. The value of viscosity extracted by fitting the time-dependence of the area to the form obtained here is consistent with those measured in independent experiments [4]. The value of η (the coefficient of drag by the solid surface on the liquid film) is obtained to be of the same order of magnitude as that found by Persson and Tosatti

Let us take the geometry to be circular of radius r_0 . The plates, confining the fluid are taken to be smooth and devoid of any imperfections. Let P_0 be the normal force applied to squeeze out the fluid. Let us assume that when the fluid is confined to a few molecular thickness, monomolecular layer of liquid are squeezed out one at a time as a result of the applied normal force as shown in Fig.1. This crucial assumption, the main phenomenological input in this approach, is supported by the experiment of Becker and Mugele [20]. As in the experiment of [1], the upper limit of change of liquid density ρ due to shear is 4%. So we can take the fluid to be incompressible in our model.

Suppose one monolayer is squeezed out, and let $\mathbf{v}(\mathbf{r}, t)$

*Electronic address: snandi@physics.iisc.ernet.in

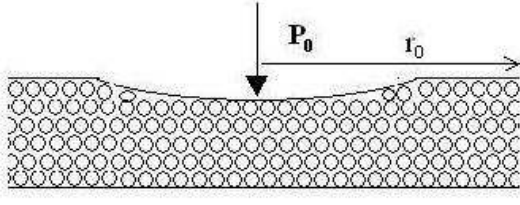


FIG. 1: The suggested flow geometry of Persson and Tosatti. The squeezing flow results in the n th layer becoming an annulus with a central hole of radius r , which spreads and pushes the rest of that layer outward, while the $(n-1)$ layers below are unaffected.

be the in-plane velocity field of this monolayer as a function of the two-dimensional in-plane coordinate \mathbf{r} and time t . Then incompressibility and the Navier-Stokes equations become:

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0 \quad (1)$$

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\frac{1}{mn_a} \nabla p + \nu \nabla^2 \mathbf{v} - \eta \mathbf{v} \quad (2)$$

where, p is the two-dimensional pressure, ν is the kinematic viscosity, η is the coefficient of drag force by the sheets on the fluid, mn_a is the two dimensional mass density.

The flow is very slow, so we ignore inertia in Eq. (2). The suggested flow geometry of Persson and Tosatti is that the squeezing flow results in the n th layer becoming an annulus with a central hole of radius r , which spreads and pushes the rest of that layer outward, while the $(n-1)$ layer below are unaffected. Then

$$\mathbf{v} = v(r, t) \hat{r} \quad (3)$$

$$p = p(r, t). \quad (4)$$

Using Eq. (3) in Eq. (1) we get,

$$\frac{1}{r} \frac{\partial}{\partial r} (rv) = 0 \quad (5)$$

or,

$$\frac{v}{r} + \frac{\partial v}{\partial r} = 0. \quad (6)$$

Equation (2) becomes

$$\frac{\partial v}{\partial t} = -\frac{1}{mn_a} \frac{\partial p}{\partial r} + \nu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v}{\partial r} \right) - \eta v, \quad (7)$$

where symmetry implies only the radial component is non-zero.

At this point, [8] makes a mistake by making the viscosity term, i.e. the second term in right hand side of

Eq. (7), to be equal to zero using Eq. (6). But this term should actually be equal to $\nu \frac{v}{r^2}$. Using this value Eq. (7) becomes

$$\frac{\partial v}{\partial t} = -\frac{1}{mn_a} \frac{\partial p}{\partial r} + \nu \frac{v}{r^2} - \eta v \quad (8)$$

From Eq. (6), we get

$$\dot{r} = v = \frac{B(t)}{r} \quad (9)$$

$$\frac{\partial v}{\partial t} = \frac{\dot{B}}{r}, \quad (10)$$

where $B(t)$ is an integration constant, which depends only on t . Now using the above two results in Eq. (8) we get,

$$\frac{\partial p}{\partial r} = -mn_a \frac{(\dot{B} + \eta B)}{r} + mn_a \nu \frac{B}{r^3} \quad (11)$$

In solving this equation, let us take the boundary condition as $p=p_0$ at $r=r_0$. Then,

$$p(r) - p_0 = -mn_a (\dot{B} + \eta B) \ln\left(\frac{r}{r_0}\right) - \frac{mn_a \nu B}{2} \left(\frac{1}{r^2} - \frac{1}{r_0^2}\right) \quad (12)$$

Now using Eq. (9) and Eq. (10), the above equation can be written as

$$p(r) - p_0 = -\frac{mn_a \eta}{4} \frac{d}{dt} (r^2) \ln\left(\frac{r^2}{r_0^2}\right) - \frac{mn_a \nu}{4} \frac{d}{dt} (r^2) \left(\frac{1}{r^2} - \frac{1}{r_0^2}\right). \quad (13)$$

Since r varies very slowly, we have ignored the second order time derivative of r^2 . Now let us take $\pi r^2 = A$ and $\pi r_0^2 = A_0$. Then,

$$\frac{dA}{dt} \ln\left(\frac{A}{A_0}\right) + \frac{\nu \pi}{\eta} \frac{dA}{dt} \left(\frac{1}{A} - \frac{1}{A_0}\right) = -\frac{4\pi(p-p_0)}{mn_a \eta} \quad (14)$$

Solving the above equation, assuming that p is independent of r , we get

$$\frac{A}{A_0} \ln\left(\frac{A}{A_0}\right) - \frac{A}{A_0} + \frac{\nu \pi}{\eta A_0} \ln(A) - \frac{\nu \pi A}{\eta A_0^2} = -\frac{4\pi(p-p_0)t}{mn_a \eta A_0} + c \quad (15)$$

where c is a constant of integration which must be evaluated from the boundary condition. Let $t = t^*$ be the time at which the whole layer is squeezed out. Then for $t = t^*$, $A=A_0$ and putting this value in the above equation we will have,

$$\left(\frac{A}{A_0} + \frac{\nu \pi}{\eta A_0}\right) \ln\left(\frac{A}{A_0}\right) + \left(1 - \frac{A}{A_0}\right) \left(1 + \frac{\nu \pi}{\eta A_0}\right) = \frac{4\pi P_0 a}{mn_a \eta A_0} (t^* - t) \quad (16)$$

Now the adiabatic work required to squeeze out one monolayer of fluid will be equal to $(p-p_0)A$. This adiabatic work must be equal to the change in free energy due to the process. The total change in free energy is $(2\gamma_{sl} + V_{ll} - 2\gamma_{sl} + P_0 a)A - V_{ll}A$, where γ_{sl}

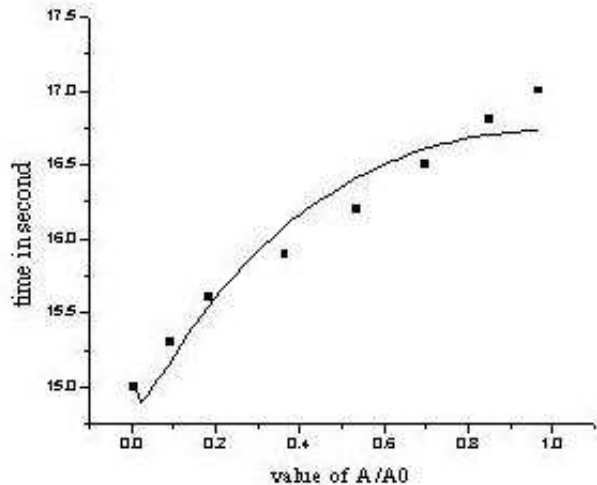


FIG. 2: The fit of Eq. (16) to the time sequence of squeezed area. The data were obtained from a time sequence picture of the squeezed area in the paper of Becker and Mugele. The filled squares are the data points and the solid curve is the equation fit to the data.

is the solid-liquid interfacial term, V_{ll} is the van der Waals interaction term. Equating these two terms we get $(p - p_0) = P_0 a$.

Now Eq. (16) gives the relation between the area of the squeezed layer as a function of time. From experiments P_0 , A_0 , t^* and the three dimensional density, all are known. So if we can take a time trace of the area of the squeezed monolayer, then by fitting equation (16) to that data with η and ν as two fitting parameters, in principle, we can have a value of both η and ν . So calculating η and ν is a matter of having good data.

Now such good data is lacking in the literature. So, we took a time-sequence of pictures of the squeezing out of one mono-layer of OMCTS in the paper by Becker and Mugele [20]. We obtained the area A of the squeezed layer as well as the total area A_0 of the mica sheets by an area-calculating software. Lacking an absolute estimate of the areas, we extracted $\frac{A}{A_0}$ from the pictures, thus obtaining the time-evolution of $\frac{A}{A_0}$. We took P_0 as the maximum applied normal pressure $P_0 \sim 2 \times 10^7 \text{ N/m}^2$ and $A_0 = 7 \times 10^{-9} \text{ m}^2$. These are the typical values of P_0 and A_0 [4, 20, 21] used in the experiments.

With the values of the parameters quoted above we fitted Eq. (16) to the obtained data, shown in Fig.2. The fit was not very good, since there are two parameters and only 8 data-points, but it was as much as could be done with the available information. The fit gave the values of $\eta \sim 7 \times 10^{14} \text{ s}^{-1}$ and $\nu \sim 4 \times 10^5 \text{ cm}^2/\text{s}$. The value of η is essentially same as that obtained by Persson and Tosatti. For comparison, the kinematic viscosity of OMCTS in

bulk is $0.02 \text{ cm}^2/\text{s}$. The value of ν from the fit is of the same order of magnitude as that for confined OMCTS in the experiments of [1, 15]. The experiments of [20] thus indicate an enhancement of viscosity by about ~ 7 orders of magnitude. The above result is interesting in at least two senses.

(a) This is an approximate calculation and can not be expected to give quantitatively accurate results. In this sense it is reassuring that a fit to our theory gives a value for ν very similar to that in independent experimental measurements. Crude approximations of layer-by-layer flow and p independent of r are made to simplify the model, and the dependence of viscosity on the film thickness can not be calculated from the model. But at molecular thicknesses a liquid film supports a state of normal stress and the film thickness adjusts itself to the externally applied normal pressure. So, in this sense, the thickness and the normal pressure are not two independent parameters.

(b) From Eq.(16), we see that one of the reasons of high increase of the value of ν is the strong wall fluid interaction. The viscosity is directly related to the relaxation time of a fluid and in the simulation of Scheidler, Kob and Binder [7], it is indeed found that the nature of the confining walls directly affects the dynamics of the fluid.

In comparison with the results obtained by Persson and Tosatti [8], we see that the value of η is almost same as in their calculation. Using the values of the different parameters, noted above, $\eta \sim 10^{14}$. But the value of ν was not obtained by their (incorrect) calculation. The model is more interesting than their calculation showed it to be, because it tells us that ν can be extracted from the experiments as well.

The theoretical approach presented here and, hence, the assumption of layer-by-layer flow, can be tested by comparison with experiments in which the area squeezed out is measured carefully as function of time. In addition, different surface treatments should give different degrees of anchoring and hence different values of η , the coefficient of surface drag. The trends predicted by Eq. (16) with respect to changes in η can then be compared with experiment.

The results presented here show that though the model is very simple and unable to explain the phenomenon completely, it nonetheless demands at least a little attention.

Acknowledgments

Finally, I would like to express my gratitude to Professor Sriram Ramaswamy for his helpful, important and enthusiastic discussions, suggestions and comments.

-
- [1] Hsuan-Wei Hu, George A. Carson and Steve Granick, Phys. Rev. Lett., **66**, 2758 (1991).
 - [2] A. L. Demirel and S. Granick, Phys. Rev. Lett., **77**, 2261 (1996).
 - [3] Hsuan-Wei Hu and Steve Granick, Science, **258**, 1339 (1992).
 - [4] John Van Alsten and Steve Granick, Phys. Rev. Lett., **61**, 2570 (1988).
 - [5] S. T. Cui, C. McCabe, P. T. Cummings and H. D. Cochran, J. Chem. Phys., **118**, 8941 (2003).
 - [6] S. T. Cui, P. T. Cummings and H. D. Cochran, J. Chem. Phys., **114**, 7189 (2001).
 - [7] P. Scheidler, W. Kob and K. Binder, Europhys. Lett., **59**, 701 (2002).
 - [8] B. N. J. Persson and E. Tosatti, Phys. Rev. B, **50**, 5590 (1994).
 - [9] S. Zilberman, B. N. J. Persson, A. Nitzan, F. Mugele and M. Salmeron, Phys. Rev. E, **63**, 055103(R) (2001).
 - [10] M. Urbakh, L. Daikhin and J. Klafter, Phys. Rev. E, **51**, 2137 (1995).
 - [11] J. Klein and E. Kumacheva, Science, **269**, 816 (1995).
 - [12] P. A. Thompson, Gray S. Grest and M. O. Robbins, Phys. Rev. Lett., **68**, 3448 (1992).
 - [13] M. Schoen, S. Hess and D. J. Diestler, Phys. Rev. E, **52**, 2587 (1995).
 - [14] J. Gao, W. D. Luedtke and U. Landman, Phys. Rev. Lett., **79**, 705 (1997).
 - [15] Yingxi Zhu and Steve Granick, Phys. Rev. Lett., **93**, 096101 (2004).
 - [16] Carolyn R. Nugent, Hetal N. Patel and Eric R. Weeks, cond-mat/0601648.
 - [17] Moumita Das, Ph.D. Thesis, Indian Institute of Science (2004).
 - [18] David R Reichman and Patrick Charbonneau, J. Stat. Mech. P05013 (2005).
 - [19] Walter Kob, *Supercooled liquids, the glass transition, and computer simulations, 2002 Lecture Notes for Les Houches 2002 Summer School - Session LXXVII: Slow Relaxations and Nonequilibrium Dynamics in Condensed Matter* p 47 [cond-mat/0212344].
 - [20] Thomas Becker and Frieder Mugele, Phys. Rev. Lett., **91**, 166104-1 (2003).
 - [21] M. L. Gee, P. M. McGuiggan, J. N. Israelachvili and A. M. Homola, J. Chem. phys., **93**, 1895 (1990).